

# UK Patent Application

(19) GB (11) 2 210 468 A

(43) Date of printing by UK Office 07.06.1989

(21) Application No 8823118.8  
(22) Date of filing 01.04.1987  
(30) Priority data  
(31) 8608115 (32) 03.04.1986 (33) GB  
(86) International application data  
PCT/GB87/00221 En 01.04.1987  
(87) International publication data  
WO87/06021 En 08.10.1987

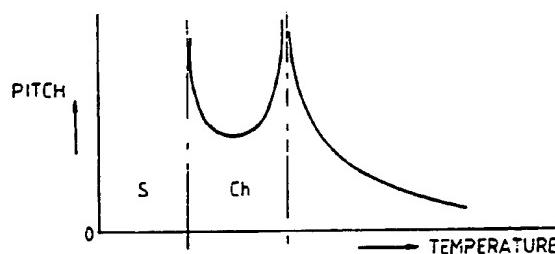
(51) INT CL' (as given by ISA)  
G02F 1/137  
(52) UK CL (Edition J)  
G2F FCD F23E F24T F25A F25F F25P2 F28M  
(56) Documents cited by ISA  
EP 0160302 A EP 0156726 A EP 0091637 A  
EP 0008956 A  
(58) Field of search by ISA  
INT CL' G02F 1/00

(71) Applicant  
The Secretary of State for Defence  
Whitehall, London, SW1A 2HB, United Kingdom  
(72) Inventors  
Madeleine Joan Bradshaw  
Edward Peter Raynes

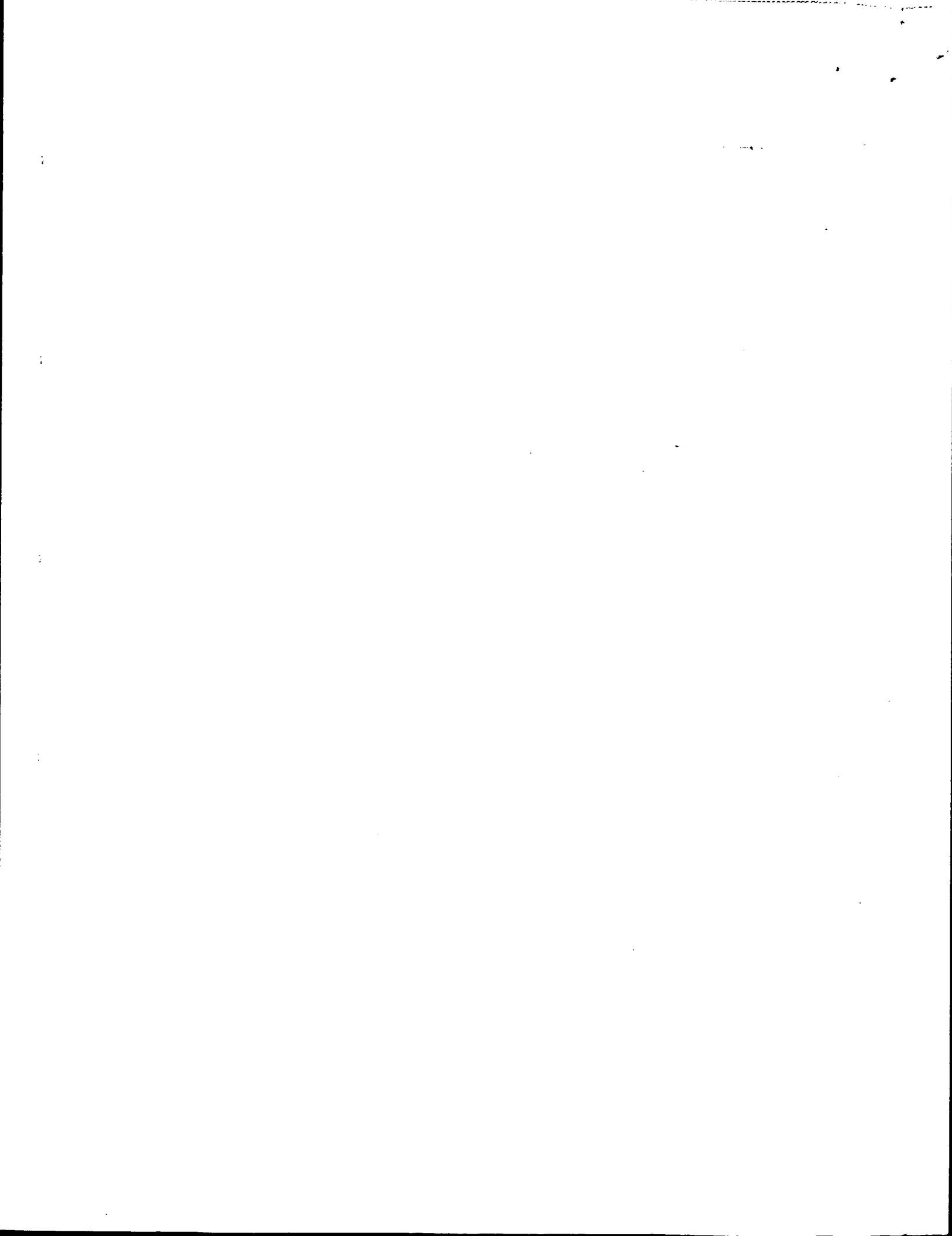
(74) Agent and/or Address for Service  
R W Beckham  
Procurement Executive Patents 1A(4),  
Ministry of Defence,  
Room 2014 Empress State Building, Little Road,  
London, SW6 1TR, United Kingdom

## (54) Smectic liquid crystal devices

(57) A liquid crystal display (1, 20) is arranged to provide very low minimum light transmission in one of its two switchable states. This makes it useful for a shutter (Fig. 1) and for high contrast digital displays (Fig. 2). A layer (14) of a chiral smectic liquid crystal material is contained between two cell walls (9, 10) carrying electrode structures (11, 12). The liquid crystal material has the following phases with temperature: isotropic cholesteric chiral smectic solid. The cholesteric pitch is large. The cell walls are surface treated to provide a parallel alignment of liquid crystal molecules. Cross polarisers (2, 3) are arranged either side of the cell walls, one (2) aligned with its optical axis parallel to the surface alignment of the adjacent cell wall (9). The device is switched (5, 5) by means of +/- d.c. voltage pulses and utilises the ferro electric effect.



GB 2 210 468 A



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : <b>G02F 1/137</b>		A1	(11) International Publication Number: <b>WO 87/06021</b> (43) International Publication Date: 8 October 1987 (08.10.87)
<p>(21) International Application Number: PCT/GB87/00221 (22) International Filing Date: 1 April 1987 (01.04.87) (31) Priority Application Number: 8608115 (32) Priority Date: 3 April 1986 (03.04.86) (33) Priority Country: GB</p> <p>(71) Applicant (<i>for all designated States except US</i>): THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND [GB/GB]; Whitehall, London SW1A 2HB (GB).</p> <p>(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>) : BRADSHAW, Madeline, Joan [GB/GB]; Underleaf, Upleadon, Gloucestershire GL18 1EJ (GB). RAYNES, Edward, Peter [GB/GB]; 23 Leadon Road, Hall Green, Malvern, Worcestershire (GB).</p>		<p>(74) Agent: BECKHAM, Robert, William; Procurement Executive, Ministry of Defence, Patents 1A(4), Room 2014, Empress State Building, Lillie Road, London SW6 1TR (GB).</p> <p>(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US.</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: SMECTIC LIQUID CRYSTAL DEVICES</p>			
<p>(57) Abstract</p> <p>A liquid crystal display (1, 20) is arranged to provide very low minimum light transmission in one of its two switchable states. This makes it useful for a shutter (Fig. 1) and for high contrast digital displays (Fig. 2). A layer (14) of a chiral smectic liquid crystal material is contained between two cell walls (9, 10) carrying electrode structures (11, 12). The liquid crystal material has the following phases with temperature: isotropic <math>\rightleftharpoons</math> cholesteric <math>\rightleftharpoons</math> chiral smectic <math>\rightleftharpoons</math> solid. The cholesteric pitch is large. The cell walls are surface treated to provide a parallel alignment of liquid crystal molecules. Crossed polarisers (2, 3) are arranged either side of the cell walls, one (2) aligned with its optical axis parallel to the surface alignment of the adjacent cell wall (9). The device is switched (5, 5) by means of +/- d.c. voltage pulses and utilises the ferro electric effect.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT Austria	FR France	ML Mali
AU Australia	GA Gabon	MR Mauritania
BB Barbados	GB United Kingdom	MW Malawi
BE Belgium	HU Hungary	NL Netherlands
BG Bulgaria	IT Italy	NO Norway
BJ Benin	JP Japan	RO Romania
BR Brazil	KP Democratic People's Republic of Korea	SD Sudan
CF Central African Republic	KR Republic of Korea	SE Sweden
CG Congo	LI Liechtenstein	SN Senegal
CH Switzerland	LK Sri Lanka	SU Soviet Union
CM Cameroon	LU Luxembourg	TD Chad
DE Germany, Federal Republic of	MC Monaco	TG Togo
DK Denmark	MG Madagascar	US United States of America
FI Finland		

- 1 -

### SMECTIC LIQUID CRYSTAL DEVICES

The invention relates to smectic liquid crystal devices.

Liquid crystal devices commonly comprise a thin layer of a liquid crystal material contained between two glass plates or walls. A  
5 thin transparent electrode is deposited on the inner face of both walls. The combination of liquid crystal layer, walls, and electrode is often termed a liquid crystal cell. When an electric field is applied between the two electrodes, liquid crystal molecules rotate in the field to an ON state. On removal of the  
10 field the molecules rotate back to an OFF state, determined by a surface treatment applied to the walls before cell assembly and by the type of liquid crystal material. The optical transmission characteristics of the ON and OFF states are different. Some devices need one or two polarisers and/or dyes to visibly  
15 distinguish between ON and OFF states.

There are broadly three different types of liquid crystal material, nematic, cholesteric, and smectic, each distinguished by a  
20 different molecular ordering.

Such materials only show a liquid crystal phase over a limited temperature range between the solid and isotropic liquid phases. Within the liquid crystal phase temperature range a material may exhibit one or more of the nematic, cholesteric or smectic phase  
25 types. Normally a material is chosen such that it forms only one type of liquid crystal phase over its working temperature range.

- 2 -

The present invention concerns devices using smectic liquid crystal materials.

Displays have been made with the electrodes formed into rows on one  
5 wall and columns on the other wall. These collectively form an x,  
y matrix of separately addressable elements on a large display.  
One type of display uses the ON and OFF states to form an  
electrically switchable optical shutter. Yet another type of  
display is used as an optical storage device. Nematic  
10 cholesteric and smectic liquid crystal material have been used for  
such devices. A problem with many displays is the time taken to  
switch between the two states i.e. the response times. For many  
displays a fast response time is needed. A nematic material,  
arranged in a 90° twisted structure typically has a response time  
15 of 100 milliseconds.

Devices comprising smectic materials have not been used as widely  
as devices with nematic or cholesteric materials. Available  
display devices based on smectic materials do not have the  
20 necessary characteristics. Recently however the smectic ferro  
electric property with its fast switching and bistability  
characteristics has become important see for example N A Clark & S  
T Lagerwall, App. Phys. Letters 36 (11) 1980 pp 899-901. Chiral  
liquid crystal materials in a tilted smectic phase, eg  $S_C^*$ ,  $S_I^*$ ,  
25  $S_F^*$ ,  $S_H^*$ ,  $S_J^*$ ,  $S_G^*$ , are known to exhibit ferroelectric properties.  
This has been described by R B Meyer, L Liebert, L Strzelecki and P  
Keller, J de Physique (Lett), 36, L-69 (1975).

- 3 -

- One problem with liquid crystal devices when used as a shutter is the amount of light that leaks through in its minimum transmission states. For example a twisted nematic cell may let through a minimum of about 1% of light. Reducing the minimum light
- 5 transmission is highly desirable for shutter applications. Also it is useful in other displays for contrast enhancement. A further problem with twisted nematic displays and shutters is their narrow angle of view; when viewed away from the normal to a display the information displayed can be corrupted.
- 10 Ideally a liquid crystal shutter should have fast response times and a very low minimum light transmission. For a digital display the display should have high contrast and a wide angle of view.
- 15 The present invention overcomes some of the above problems to provide a fast shutter with low minimum light transmission by the smectic ferro electro property together with a careful alignment of the liquid crystal molecules and polarisers, and selection of liquid crystal material characteristics.
- 20

- 4 -

According to this invention a liquid crystal device capable of being switched into two states comprises  
a layer of a tilted chiral smectic liquid crystal crystal material contained between two cell walls each carrying electrodes and  
5 surface treated to give homogeneous alignment to the liquid crystal molecules, the alignment directions being parallel or near parallel  
and two polarisers arranged either side the cell wall faces and  
with the optical axis of one polariser crossed with respect to  
10 the optical axis of the other polariser and with optical axis of one polariser parallel to liquid crystal molecular alignment in one of their switched states  
the liquid crystal material having a tilted chiral smectic phase at normal device operating temperatures and a cholesteric  
15 phase at a higher temperature, with a cholesteric pitch of at least the layer thickness in the cholesteric phase at least 0.1°C above the cholesteric to smectic transition temperature, a substantial spontaneous polarisation coefficient and the following phases with increasing temperatures:-  
20 chiral smectic - cholesteric - isotropic.

The alignment directions on the two walls may be parallel in the same or opposite directions, ie parallel or antiparallel.

- 5 -

A method of making a liquid crystal display device according to this invention comprises the steps;

providing two cell walls spaced apart by a spacer to contain a layer of a liquid crystal material, the wall inner surfaces having formed thereon electrode structures and surface treated to provide a homogeneous liquid crystal alignment,

5 providing a tilted chiral smectic liquid crystal material having a cholesteric phase at an elevated temperature between the chiral smectic and isotropic phases with a cholesteric pitch  $p$  greater than half the layer thickness  $d$  at a temperature at least  $0.1^{\circ}\text{C}$  above a cholesteric to smectic transition temperature and a significant spontaneous polarization  $P_s$  in the chiral smectic phase,

10 heating the mixture to the cholesteric phase, introducing and sealing the mixture into the space between the walls,

15 cooling the material to the tilted chiral smectic phase arranging the cell walls between two linear polarisers with at least one polariser having its polarisation axis parallel 20 to an adjacent molecular alignment direction.

- 6 -

The liquid crystal material may be a single component or a mixture of components. The material may combine one or more chiral components with laevo (left hand) cholesteric twist sense with one or more chiral components with dextro (right hand) cholesteric 5 twist sense. With such a mixture none of the laevo components can be the racemates of the dextro components. This chiral mixture may be a chiral smectic itself or may be used as an additive to a non-chiral and/or racemate smectic liquid crystal host material. Alternatively the chiral component or components may have the same 10 cholesteric twist sense providing the cholesteric pitch and  $P_s$  have the above values. The material has the following phases:-  
isotropic - cholesteric (or nematic) - smectic\*.

The smectic phase has at least one of the following chiral smectic 15 phases C\*, I\*, F\*, J\*, G\*, K\*, H\* depending on temperature.

The p/d ratio is large enough to prevent the material, in its cholesteric phase, adopting more than a  $3\pi$  twist, ideally the pitch  $p$  is greater than  $4d$ , above the cholesteric to smectic phase 20 transition, so that much less than  $\pi$  twist can occur in the cholesteric phase near the transition. Ideally this value of  $p$  is large over the whole cholesteric phase, preferably is large for  $5^\circ\text{C}$  above the chiral/cholesteric transition.

25 The pitch in the smectic phase is greater than  $1 \mu\text{m}$  and preferably much greater, e.g. greater than layer thickness. The layer thickness,  $d$ , may be up to  $15 \mu\text{m}$ .

Prior art chiral smectic devices have a smectic A phase between the 30 cholesteric and S\* phase. Alignment is assisted by slow cooling from the cholesteric phase. It was not possible to obtain uniform alignment without a smectic A phase. The present invention permits good device alignment without an SA phase being present. This arises because of the compensated or long cholesteric pitch in 35 the cholesteric phase.

- 7 -

The value of  $P_s$  is at least 0.1 and preferably 1 or more  $nC/cm^2$ . All the chiral components may have substantial values of  $P_s$  and the same sense of  $P_s$ . Alternatively one or more components may have  $P_s$  values of opposite senses providing the net  $P_s$  is substantial.

5

For some materials the cooling is at a rate of between  $0.05^\circ$  and  $2^\circ C$  /minute within +/-  $5^\circ C$  of the cholesteric to smectic phase transition. However, when the cholesteric pitch is large, i.e. the material is well compensated or is naturally of long pitch the 10 device may be cooled as rapidly as is convenient, e.g.  $20^\circ C/\text{minute}$  or more.

15 The device may further include means for applying two d.c. voltages of opposite polarity to the electrode structures whereby the molecules of the mixture are forced to lie in one of two different positions depending on the polarity of applied voltage and switch between these two positions as the polarity is changed.

20 According to this invention a liquid material mixture for use in a tilted chiral smectic liquid crystal device comprises a material having a chiral smectic phase at normal device operating temperatures and a cholesteric phase at an elevated temperature,

25 the mixture having a cholesteric pitch greater than  $2d$  in the cholesteric phase at least  $0.1^\circ C$  above a cholesteric to smectic transition temperature, and a substantial polarisation coefficient  $P_s$ , in the smectic phase.

30 Preferably the pitch in the cholesteric phase is much greater than  $4\mu m$  and ideally approaches infinite pitch.

The device ambient or operating temperature typically falls within the range of  $0^\circ$  to  $40^\circ C$  although when used on equipment it may reach  $100^\circ C$ .

35

- 8 -

The mixture may include an amount of a pleochroic dye.

Use of chiral components in nematic liquid crystal material is well known. The addition of a chiral component imparts a twist direction to the nematic material director and results in a cholesteric material. The direction of this twist can either be clockwise or anticlockwise, i.e. right or left rotation. Adding two different chiral materials of opposite twist can result in zero twist depending upon the composition and temperature of the mixture. Some compounds can have molecules with both right and left rotatory power, these are optical isomers when the optical isomers are present in equal amounts a racemic mixture is formed which is indistinguishable from ordinary non-chiral liquid crystalline materials.

15

#### Brief Description of the Drawings

One form of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:-

20 Figure 1 is a sectional view of a liquid crystal shutter system for a film camera;

Figure 2 is a view of a four character eight bar display;

Figures 3 a, b are respectively a stylised plan and sideview of a layer of tilted chiral smectic liquid crystal material;

25 Figure 4 is an enlarged view of part of Figure 3 showing two switched states;

Figures 5 a, b, c are graphs of cholesteric pitch versus temperature for various mixtures.

30

- 9 -

The shutter system of Figure 1 comprises a liquid crystal cell 1 arranged between crossed first and second polarisers 2, 3, aligned as described below.

- 5 In front of the first polariser 2 is a light sensor 4 e.g. a photo diode. Control of the cell 1 is from a control unit 5 which receives signals from the sensor 4 and voltage from a voltage source 6 e.g. a 12 volt battery. Behind the cell 1 is a lens system 7 focussing light onto a photographic film 8 or other detector, the cell 1 can be switched between light transmissive and opaque states as explained later.
- 10

The cell 1 comprises two glass walls 9, 10 carrying sheet electrodes 11, 12 e.g. 100 $\text{\AA}$  thick tin oxide. A spacer ring 13 seals a layer 14 of liquid crystal material between the walls 9, 10. Small strands (not shown) of glass fibres distributed throughout the layer may be used to improve the accuracy of cell wall spacing. A typical layer 14 thickness is 2 to 12  $\mu\text{m}$ . Prior to assembly the walls 2, 3 are surface treated by spinning on a thin layer of polyamide or polyimide, drying and where appropriate curring; then buffing with a soft cloth (e.g. rayon) in a single direction R1, R2. As shown the directions R1, R2 are antiparallel but may be parallel in the same direction. This known treatment provides a surface alignment for liquid crystal molecules. The molecules align themselves along the rubbing direction R1, R2, and at an angle of about 2° to the surface. Alternatively SiOx may be obliquely evaporated onto walls to provide alignment.

- 10 -

Thus to expose the film 8 to a scene by flash light the cell 1 and polariser 2, 3 forming a shutter is triggered open and shut by the sensor 4 and control unit 5 to correctly expose the film 8.

Alternatively, if the cell 1 is used to protect e.g. a television phototube, the cell 1 would normally be in its transmissive state and switched to opaque if incident light was too great for the tube.

Figure 2 shows a four digit eight-bar display 20. This comprises a liquid crystal cell provided with electrodes 21 shaped to provide a known eight-bar display as described in G.B. Patent Specification No. 2 009 219 and 2 031 010. Suitable voltages are switched by a driver control 22 from a battery 23 to display numbers from zero up to 9,999. The display 20 is constructed as in Figure 1 with a cell arranged between two polarisers.

The digital display may be viewed by reflection of ambient light in which case a reflector is arranged behind the display. Alternatively the display may be back lit e.g. by a tungsten bulb. In some cases the reflector may be partly transmissive so that the display can be viewed both by reflective and transmitted light.

- 11 -

Alignment and switching of the liquid crystal layer will now be described with reference to Figures 3, 4, 5. The layer 14 of liquid crystal material is a chiral smectic material e.g. smectic C\*. A non-chiral smectic material forms itself into micro-layers 5 normal to the wall with molecules 26 lying normal to the micro-layer. This is analogous to fibres in a fibre optic plate. Chiral smectic materials arrange themselves with the molecules 26 at a small angle to the normal of the micro layers 25 as shown in Figure 10 3a. The wall surface alignment treatment provides a strong alignment to molecules in contact therewith.

As a result the molecules 26 align, at the wall surface, along a rubbing direction R and the micro layers 25 form at a typical angle of 70° to the rubbing direction.

15 To provide a uniform alignment of both molecules 26 and micro-layers 25 it is necessary to use a smectic material with a cholesteric phase at elevated temperatures. Figure 5a shows a cholesteric pitch p versus temperature curve for a typical 20 conventional smectic material with a cholesteric phase. As the temperature reduces very close to a cholesteric/smectic phase transition, pitch p increases towards infinity. Away from this transition cholesteric pitch becomes very small, typically much less than 1  $\mu\text{m}$ .

25

- 12 -

Displays of the present invention have a long pitch in the cholesteric phase for at least 0.1°C above this phase transition. Preferably this range is 5°C and ideally occurs over the whole cholesteric temperature range. Within this range the minimum p is 5 greater than 4d, d being the layer thickness.

- There are a number of ways of achieving the above material. For example combining one or more chiral components with laevo (left) cholesteric twist sense with one or more chiral components with 10 dextro (right) cholesteric twist sense, with the proviso that none of the laevo components are the racemates of the dextro components. Such a mixture may be used by itself if it has the necessary smectic phases. Alternatively the chiral mixture may be added to a non-chiral or a racemate liquid crystal material, eg a smectic C 15 host. Different chiral components may have different temperature/pitch characteristics. In this case it is necessary to ensure that the resultant pitch has the required value in the temperature range above the smectic/cholesteric phase transition.
- 20 When using chiral components of opposite twist sense it is necessary to ensure that the resultant mixture has the required spontaneous polarization value Ps. Thus all of the chiral components, regardless of their cholesteric twist sense, may have the same sense of S \* polarization, i.e. their Ps add.
- 25 Alternatively one or more of the chiral components may have the opposite sense of Ps providing the net Ps has a sufficient value.

- 13 -

Another way of achieving the above material is to use one or more chiral components with the same cholesteric twist sense and S \* polarisation sense but still satisfying the cholesteric pitch values noted above. Such a mixture may be used alone or in combination with a non-chiral or a racemate liquid crystal material, eg a S<sub>C</sub> host.

As a result of the long pitch in the cholesteric phase the material 10 cools into the S<sub>C</sub>\* phase with uniform alignment caused by the cell wall treatment. The result is alignment as in Figure 3.

The pitch in the smectic phase is arranged to be greater than about 1  $\mu\text{m}$  and preferably very much greater.

15 The compensation of pitch in the cholesteric phase is illustrated in Figures 5(a), (b), (c). Figure 5(a) shows cholesteric pitch against temperature for a noncompensated material having a cholesteric to smectic transition. At this transition the pitch tends to infinity. The compensated material shown in Figure 5(b) 20 shows a pitch increase a few degrees above the transition temperature with a pitch reduction below. By suitable selection of materials this pitch increase can be made to occur even closer to the transition temperature as in Figure 5(c), but a few degrees difference does not seem to affect the end result. Some 25 materials, e.g. Examples 4, 5 below, show a long pitch cholesteric characteristic over the whole cholesteric temperature range with a single chiral dopant. These are inherently good materials as in Figure 5(c) without the need for compensation as shown in Figure 5(b).

30

- 14 -

To obtain the uniform alignment of Figure 3 the liquid crystal material in the cell is heated to about 5°C above the smectic/cholesteric phase transition. It is then cooled at a typical rate of about 0.05 and .2°C per minute within +/- 5°C of 5 the transition. In some cases the application of a d.c. voltage, e.g. 10 volts of appropriate polarity assists in obtaining uniform alignment during cooling. Additionally a material after cooling 10 into the smectic phase can be slowly heated just into the cholesteric phase and recooled whilst an appropriate voltage pulse is maintained. When the uniform alignment of Figure 3 is obtained 15 the cell 1 is ready for use. Liquid crystal molecules adopt one of two alignment direction D1, D2 depending on the polarity of an applied voltage. A typical voltage is +/- 10 volts. These two positions are seen in Figure 4 in full D1 and broken lines D2.

15 For this invention, not necessarily all chiral smectic displays, one of the two applied field D alignments is also the field OFF state. Rapid switching between the two states, when the d.c. pulses are applied, is due to the smectic ferro electric property 20 of the material. Typically the cell can be switched between D1 and D2 in about 0.5 to 1 ms. The two different directions D1, D2 represent two different directions of Ps, often termed UP and DOWN directions. These two directions D1, D2 may be about 45° apart depending on the material composition.

25 The polariser 2, or 3 is preferably aligned along the direction D which may be slightly different from direction R .

- 15 -

Because of the strong molecular alignment between crossed polarisers 2, 3, less than about 0.01% of light is transmitted through the shutter formed by the cell 1 and polarisers 2, 3 combination in its voltage OFF, i.e. the state in full lines in

5 Figure 4. When switched to the DOWN state the shutter is highly transmissive. This makes the cell of this invention very suitable for shutter systems. Also the contrast between UP and DOWN states gives enhanced eight-bar displays as in Figure 2. Additionally the display has a wide angle of view.

10

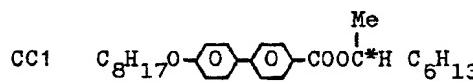
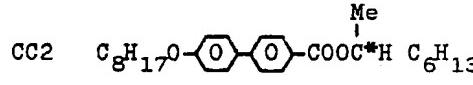
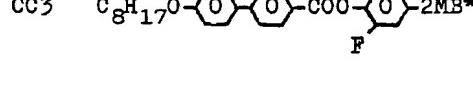
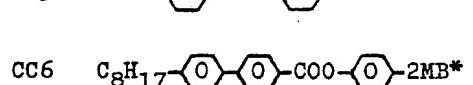
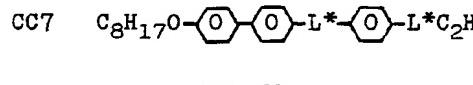
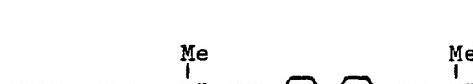
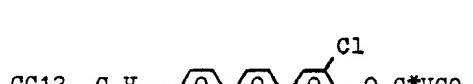
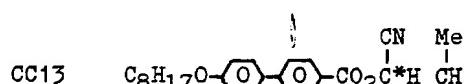
If about 1% of a dichroic dye is incorporated into the liquid crystal material 14 only one polariser is needed aligned parallel or perpendicular to one of the directions D1, D2. One example of a dye is BDH dye catalogue number D102 available from BDH, Poole, 15 England. In this case angle between D1, D2 is preferably about 90°.

Example of materials:-

Mixtures can be prepared using the following components  
20

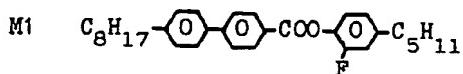
Chiral Components as described in G.B. Patent Application No. 8520715.

- 16 -

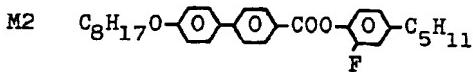
	Code	Absolute configuration S or chiral group(s)	Sense of L cholesteric twist	Sense of (+) spontaneous polarisation
5	CC1 			
10	CC2 	R	D	(-)
15	CC3 	S	D	(+)
20	CC4 	SS	D	(+)
25	CC5 	SS	D	(+)
30	CC6 	S	D	(+)
35	CC7 	SS	L	(+)
	CC8 	S	L	(+)
	CC9			
	CC12 	D		(+)
	CC13 	D		(+)
	where 2MB*:- CH2C(H)(Me)C2H5; and L* = -COO-C(H)(Me)COO-			

- 17 -

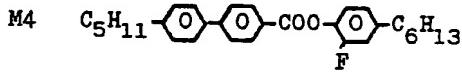
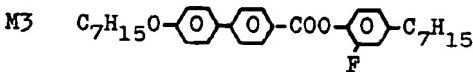
Non-Chiral Materials as in GB patent application No 8520715.



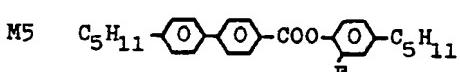
5



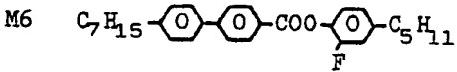
10



15

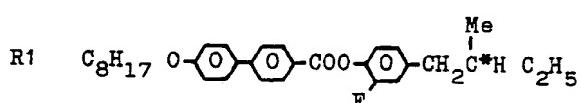


20



## Racemate Materials

25



30

- 18 -

Sc Host Mixtures

Code      Composition

H1:-	M1 + M2 + M3	(1 : 1 : 1)
H2:-	M2 + M3 + R1	(1 : 1 : 1)
5    H3:-	M1 + M6 + M4	(1 : 1 : 1)
H4:-	M2 + M3 + M5	(1 : 1 : 1)

Example 1

10    CM13:- 90% (90% H4 + 10% M7) + 10% (49% CC1 + 51% CC4)

Isotropic 135°C Cholesteric 52.3°C \* - 15°C ?.

S? means an unknown smectic phase.

15

In a 6  $\mu\text{m}$  cell, a 0 twist state was obtained for up to  $\sim 10^\circ\text{C}$  above the smectic A to cholesteric phase transition temperature. At  $30^\circ\text{C}$  the spontaneous polarisation of the mixture was  $3.4\text{nC/cm}^2$  and the tilt angle (i.e. half the cone angle) was  $21^\circ$ .

20

- 19 -

Example 2

CM15:- 15.9% (31.4% CC9 + 68.6% CC4) + 94.1% H1.

Isotropic 135°Cholesteric 56.1°S<sub>c</sub>\* 20°Solid.

5

In a 6  $\mu\text{m}$  cell, a  $\pi$  twist state was maintained for a few degrees Celcius above the smectic C\* to cholesteric transition. The alignment was poor after initially cooling into the S<sub>c</sub>\* phase, however, by applying  $\sim 20\text{Vpk}$  10Hz square wave-zero twist alignment in the smectic C\* could be induced. Heating back up to just into the cholesteric phase and cooling with a d.c. field of appropriate sign then gave the desired alignment.

10 At 50°C and 30°C the spontaneous polarisation of the mixture is 15 2nC/cm<sup>2</sup> and 6.2nC/cm<sup>2</sup>, respectively.

Example 3

Single cholesteric sense chiral component plus S host.

LPC6:- 0.5% CC + 99.5% (95% H4 + 5% M7)

20

Isotropic 152°cholesteric 76.8°S<sub>c</sub>\* <0 S?

In a 6  $\mu\text{m}$  cell, a zero twist state can be achieved for up to 0.2°C above the smectic C\* to cholesteric transition temperature.

25

- 20 -

Example 4

UCM 30:- 92.5% (85%H<sub>4</sub> + 15% M7) + 7.5% CC 12

Isotropic 155.8°C, cholesteric 60.5 C, Sc\* 15° S?

5

The cholesteric pitch-temperature curve is similar to Figure 5(c).

P<sub>s</sub> = 4.4nC/cm<sup>2</sup> at 50.5°C and 8.4nC/cm<sup>2</sup> at 25°C. In a 6.2 μm thick cell a zero twist state can be achieved for ~7°C above the Sc\* to cholesteric phase transition temperature.

10

Example 5

LPM13:- 72.5% H1 + 25% M7 + 2.5 % CC13

Isotropic 118° cholesteric 56.3° chiral smectic

15

P<sub>s</sub> = 10 nC/cm<sup>2</sup> at 20°C and 5 nC/cm<sup>2</sup> at 46°C.

This material shows zero twist in the cholesteric phase.

20

- 21 -

Claims

1. A liquid crystal device capable of being switched into two states comprising  
a layer of a tilted chiral smectic liquid crystal material contained between two cell walls each carrying electrodes and  
5 surface treated to give homogeneous alignment to the liquid crystal molecules, the alignment directions being parallel or near parallel  
and two polarisers arranged either side the cell wall faces and  
with the optical axis of one polariser crossed with respect to  
10 the optical axis of the other polariser and with the optical axis of one polariser parallel to liquid crystal molecular alignment in one of their switched states  
the liquid crystal material having a tilted chiral smectic phase at normal device operating temperatures and a cholesteric phase at a higher temperature, with a cholesteric pitch of at  
15 least the layer thickness in the cholesteric phase at least 0.1°C above the cholesteric to smectic transition temperature, a substantial spontaneous polarisation coefficient and the following phase with increasing temperatures:-  
20 chiral smectic - cholesteric - isotropic.
2. The device of claim 1 and further including means for applying d.c. pulse of appropriate polarity to the electrodes and change the state of the device between light  
25 transmissive and opaque states,  
means for measuring light falling on the device, and  
means for switching the device to a non-light transmissive state when measured light exceed a pre-determined value.

30

- 22 -

3. The device of claim 1 wherein the alignment directions on the cell walls are approximately parallel and in the same direction.

5 4. The device of claim 1 wherein the net spontaneous polarisation coefficient  $P_s$  is greater than  $0.1 \text{ nC/cm}^2$ .

5. The device of claim 1 wherein the net spontaneous polarisation coefficient  $P_s$  is greater than  $1.0 \text{ nC/cm}^2$ .

10 6. The device of claim 1 wherein the smectic pitch is greater than  $1 \mu\text{m}$ .

15 7. The device of claim 1 wherein the smectic pitch is greater than the liquid crystal layer thickness.

8. The device of claim 1 wherein the liquid crystal layer thickness  $d < 15 \mu\text{m}$ .

20 9. The device of claim 8 wherein the cholesteric pitch  $p$  is greater than  $2d$  in the cholesteric phase at least  $0.1^\circ\text{C}$  above the cholesteric to smectic phase transition.

25 10. The device of claim 8 wherein the cholesteric pitch  $p$  is greater than  $4d$  in the cholesteric phase at least  $0.1^\circ\text{C}$  above the cholesteric to smectic phase transition.

11. The device of claim 1 wherein the device operating temperature is up to  $100^\circ\text{C}$ .

30 12. The device of claim 1 wherein the device operating temperature is up to  $40^\circ\text{C}$ .

- 23 -

13. The device of claim 1 wherein the angle between liquid crystal molecule directions (D<sub>1</sub>, D<sub>2</sub>) in their two switched states is about 45°.

5 14. The device of claim 1 wherein the electrodes are formed to display digital values.

10 15. The display of claim 4 and further including a reflector for reflecting ambient light back through the liquid crystal layer and polarisers.

16. The device of claim 1 wherein one polariser is replaced by an amount of a dichroic dye in the liquid crystal material.

15

1/3

Fig. 1.

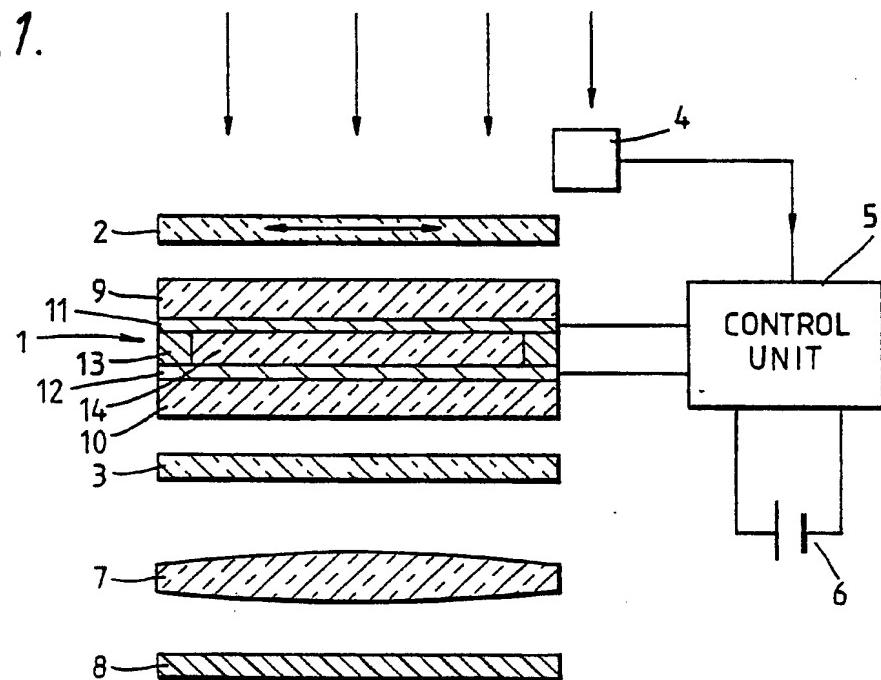
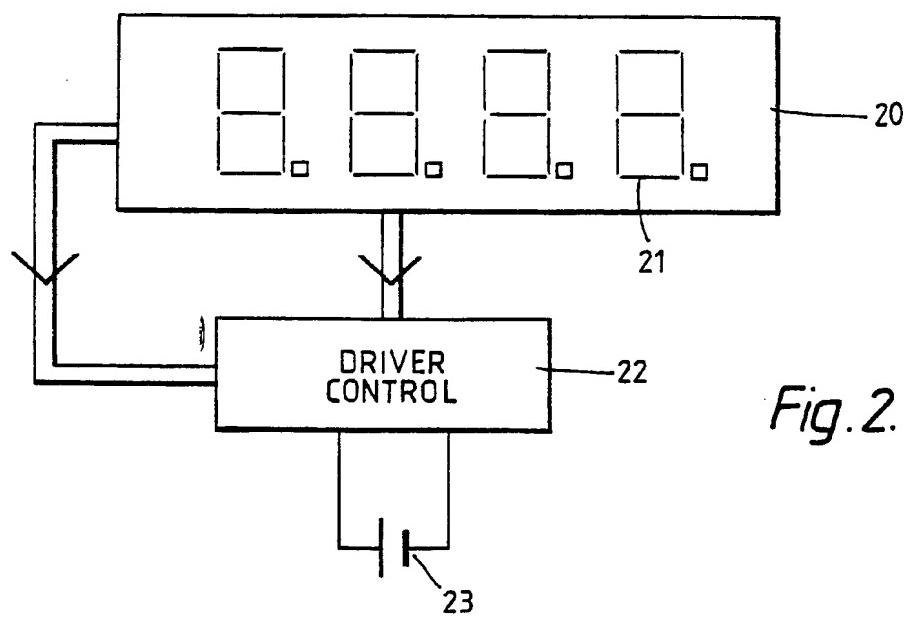
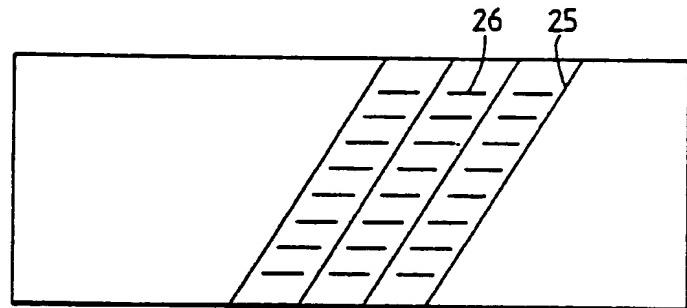
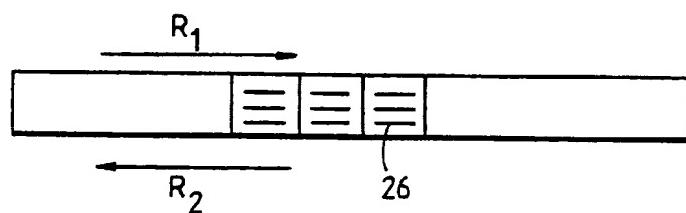
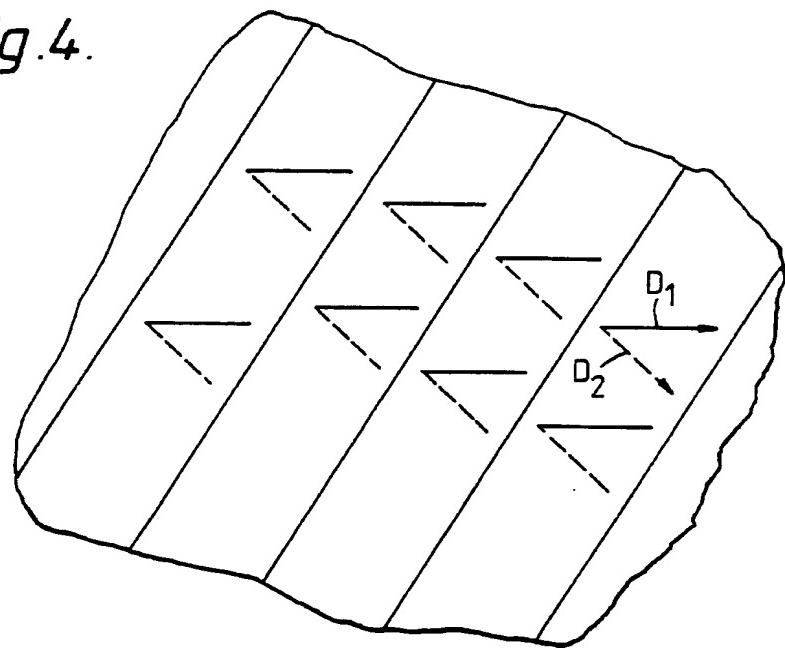


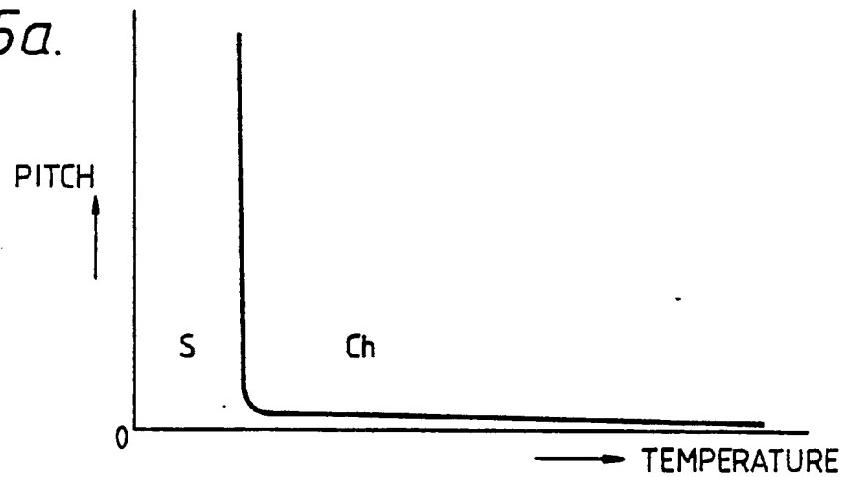
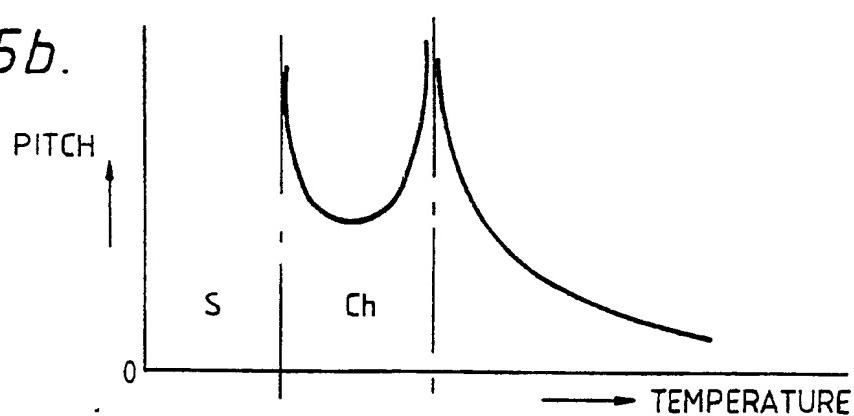
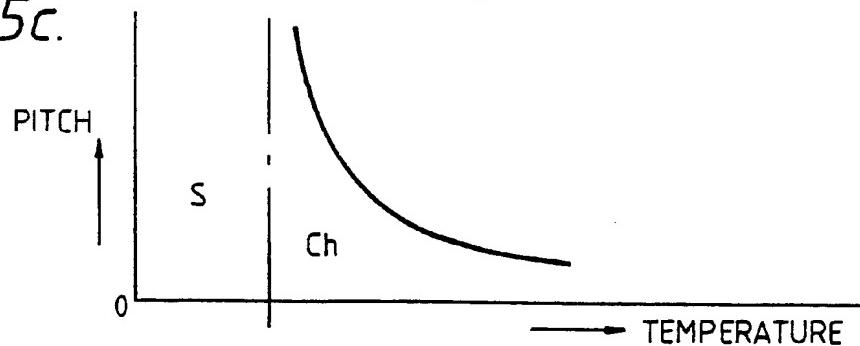
Fig. 2.



2/3

*Fig. 3a.**Fig. 3b.**Fig. 4.*

3/3

*Fig. 5a.**Fig. 5b.**Fig. 5c.*

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00221

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

**IPC<sup>4</sup>** : G 02 F 1/137

## II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System	Classification Symbols
IPC <sup>4</sup>	G 02 F 1/00

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT\*

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages ***	Relevant to Claim No. 13
A	EP, A, 0160302 (HITACHI LTD) 6 November 1985 see page 8, line 15 - page 10, line 28 --	1,6
A	EP, A, 0156726 (THOMSON-CSF) 2 October 1985 see page 2, lines 1-29; page 5, lines 1-24 --	1,6 ,8,12
A	EP, A, 0091637 (HITACHI LTD) 19 October 1983 see page 6, line 12 - page 7, line 10; page 21, line 8 - page 23, line 12 --	1,3-5,13, 15,16
A	EP, A, 0008956 (THE SECRETARY OF STATE FOR DEFENCE) 19 March 1980 see page 2, lines 4-9; page 28, lines 7-9 & GB, A, 2031010 (cited in the application)	1,15
	-----	

\* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

8th July 1987

Date of Mailing of this International Search Report

31 JUL 1987

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

M. VAN MOL

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

---

INTERNATIONAL APPLICATION NO. PCT/GB 87/00221 (SA 16660)

---

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 17/07/87

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A- 0160302	06/11/85	JP-A-	60230635	16/11/85
		US-A-	4634228	06/01/87
		JP-A-	60260923	24/12/85
EP-A- 0156726	02/10/85	FR-A-	2561657	27/09/85
		JP-A-	60223891	08/11/85
EP-A- 0091637	19/10/83	JP-A-	58173719	12/10/83
EP-A- 0008956	19/03/80	GB-A, B	2031010	16/04/80
		US-A-	4462924	31/07/84